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A FUNDAMENTAL STUDY OF A NOVEL EXTRACTION STAGE FOR AN ORGANOSOLV-BASED BLEACHING SEQUENCE

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ABSTRACT

The extent of lignin removal in a caustic extraction stage (E) of a DE bleaching sequence is severely hindered if most of the water is replaced with ethanol. However, an acidic ethanol extraction stage (A_E) may provide an alternative method to alkaline extraction for an ethanol-based organosolv bleaching sequence. We have examined the influence of A_E process variables such as ethanol concentration, acid concentration, temperature, and time on delignification of a D-stage treated pulp. An A_E-stage can remove 20 to 50% of the lignin entering the stage; the specific amount depends on the process conditions. A corresponding aqueous acid stage (A) was ineffective at lignin removal. Delignification during the A_E-stage appears to be controlled by lignin diffusion. High acid concentrations in the A_E-stage caused severe carbohydrate degradation at temperatures ≥100°C; however, the selectivity of the A_E-stage can be significantly improved through acid concentration and temperature adjustments.

Keywords: Acid, activation energy, alkaline, bleaching, carbohydrates, chemical reactions, chlorine dioxide, delignification, diffusion, ethanol, extraction, kraft pulps, kinetics, lignin, organosolv, selectivity, solubility, viscosity, zero-span.

INTRODUCTION

A major impetus for using aqueous organic solvents for chemical pulping is to produce easily bleached pulps that are comparable in strength to kraft. Processes such as Alcell®, ASAM, and organocell often utilize 15 to 70% alcohol in the pulping media [1-3]. It is believed that these organic solvents promote the dissolution of lignin and/or inhibit non-productive reactions (e.g., condensation) [1,4,5]. Recent research efforts have also examined the washing of organosolv pulps with organic solvent-water solutions. Substantial amounts of lignin are removed from Alcell® pulps if aqueous ethanol solutions are used instead of water [6]. The additional delignification was attributed to the higher lignin solubility in ethanol-water solutions than in water alone [7].

The application of organic solvent-water mixtures in chemical pulp bleaching has been recently investigated. Dramatic improvements in ozone bleaching selectivity of kraft and Alcell® pulps have been observed when ethanol-water or other aqueous organic solutions are employed [8-10]. However, most of these investigations have not examined the use of organic solvent-water in other bleaching stages. The use of organic solvent-water solutions in multiple stages may offer a selective method to easily remove residual lignin similar to organosolv pulping [11].

We have examined "organosolv bleaching" of softwood kraft pulps with the DE delignification sequence [12,13]. Poorer delignification was observed when the caustic extraction (E) was performed with high concentrations of ethanol (≥50%). These results differ from what might be expected on the basis of the results reported for organosolv pulp washing with solvent-water mixtures [6,7]. However, modifications to the residual lignin structure during chlorine dioxide treatment render the lignin fragments less soluble in ethanol-water solutions under the alkaline conditions of extraction [13].

Chlorine dioxide generates carboxylic acid functionalities on the residual lignin. In general, most carboxylic acids are more soluble in certain organic solvents, like ethanol, than in water. However, the opposite solubility behavior is observed with sodium salts of carboxylic acids [14]. Thus, it may be possible to extract the oxidized lignin fragments with ethanol under acidic conditions. The objective of this research is to fundamentally examine acid ethanol-water extraction (A_E) as an alternative method to alkaline extraction for an ethanol-based bleaching delignification sequence.

RESULTS AND DISCUSSION

Preliminary Experiments on Delignification

Several preliminary experiments were performed to establish how process conditions affected A_E delignification. Figure 1 shows the effect of ethanol concentration of the extraction liquor on delignification. Increasing the ethanol concentration facilitated lignin removal from the chlorine dioxide treated pulp. The greatest delignification occurred when the extraction media contained 90% ethanol. An almost negligible amount of lignin was dislodged from the pulp with an aqueous acid extraction (0% ethanol).

The second set of experiments examined the influence of acid concentration on A_E delignification with a 90% ethanol medium. Lignin removal was enhanced as the acid concentration (i.e., HCl) was increased from 10^{-4} to 10^{-1} M (Fig. 2). Low concentrations of acid ($\leq 10^{-3}$) appeared to have little influence on kappa number reduction.

Additional runs were performed to evaluate how temperature affected A_E lignin removal. Figure 3 indicates that lignin extraction was extremely slow at 25°C; however, increasing the temperature from 25 to 100°C strongly increased delignification. A 40% kappa number reduction occurred when the A_E-stage temperature was increased to 100°C. The kappa number appeared to decrease linearly over the temperature range examined.

The dissolution of lignin over time for the A_E-stage was examined at 70, 80, and 100°C (Fig. 4). Increasing the reaction temperature appeared to accelerate the initial kappa number drop observed during the first hour. Afterwards, delignification occurred gradually over the 1- to 5-hour reaction period for all three temperatures. A 14-hour reaction run at 100°C only showed a very slight decrease in lignin content compared to the 5-hour run (11.1 vs. 11.6 kappa, respectively).

Kinetic Analysis of Delignification

A kinetic analysis was performed on the preliminary data to assess possible controlling factors for A_E delignification. Reaction rates were calculated based on the data shown in Figures 3 and 4 using an integrated first-order rate expression with respect to the disappearance of "leachable lignin":

$$ln\left(\frac{C_L(t) - C_L(\infty)}{C_L(0) - C_L(\infty)}\right) = -kt \quad (1)$$

where k is the rate constant; t is the reaction time; $C_L(t)$ is the lignin content of the pulp at time t; $C_L(0)$ is the initial lignin concentration in the fiber wall; and $C_L(\infty)$ is the lignin concentration in the pulp at infinite reaction time (i.e., "floor level lignin"). The denominator in Equation 1 represents the initial concentration of removable lignin prior to reaction, whereas the numerator represents the remaining removable lignin at time t.

Kappa numbers were used as representations for the average lignin concentration within the fiber walls. The $C_L(\infty)$ value was estimated to be 11.1 based on the 14-hour extraction at 100°C. The pulp's entering kappa, 19.3, was equated with $C_L(0)$. Estimated rate constants based on Equation 1 are given in Table I over the 25 to 100°C temperature range. Equation 1 reasonably fits the delignification kinetics observed based on a first-order relationship with respect to leachable lignin over the 70 to 100°C range.

Table I. Calculated values for the rate constant k as a function of temperature for an A_E-stage conducted with a 90% ethanol medium with 10^{-2} M $[H^+]$.

Temperature (°C)	Rate Constant k from Eq. 1 (s^{-1})	R^2	Data Points
25	0.646×10^{-5}	1	2
40	1.12×10^{-5}	1	2
55	2.75×10^{-5}	1	2
70	3.78×10^{-5}	0.98	5
85	6.20×10^{-5}	0.99	4
100	15.0×10^{-5}	0.98	4

The rates reported in Table 1 for the 25 to 55°C range are tentative estimates based on limited data; they are included here to give an overall general conception of how the rate constant is affected by temperature. An activation energy of 8.9±1.7 Kcal/mole (± values are at the 95% confidence interval) was calculated from this data using an Arrhenius expression (Fig. 5). This activation energy is much too low to be attributed to the cleavage of covalent bonds; activation energies for ether linkages, the weakest bonds to cleave in residual lignin, are on the order of 17 to 40 Kcal/mole [15-17].

A second delignification kinetic analysis was performed to determine the contribution of the acid for an A_E-stage. The results in Figure 2, as noted earlier, showed that increasing the acid concentration in the ethanol solution facilitated lignin removal; however, delignification still occurred at very low acid concentrations ($\leq 10^{-3}$ M). A second set of experimental A_E runs was performed varying the acid concentration at 100°C at 2.5 hours (Fig. 5). There was a similar delignification profile observed for the 100°C runs as for the 70°C, namely that the delignification levels off at acid concentrations $\leq 10^{-3}$ M. In both cases, the acid concentration at the start and the end of the reactions remained relatively unchanged based on pH measurements.

These results suggested that the acid functions as a catalyst for lignin removal during the A_E-stage. A more generalized integrated rate expression can be written, which incorporates both non-catalyzed and acid-catalyzed parallel reactions:

$$ln\left(\frac{C_L(t) - C_L(\infty)}{C_L(0) - C_L(\infty)}\right) = -(k' + k''[H^+]^m)t \quad (2)$$

where k' and k'' are the rate constants for non-catalyzed and acid-catalyzed reactions; $[H^+]$ is the acid concentration; and m is an exponent. The rate constant in Equation 1, k, is an amalgamation of both k' and $k''[H^+]^m$ at an $[H^+]$ of 10^{-2} M. The temperature dependency of this overall k may not be representative of the consecutive parallel reactions occurring for delignification [18]. Thus, the following analysis was performed to assess the activation energies of the non-catalyzed and acid-catalyzed delignification reactions.

Data contained in Figures 2 and 5 were used to estimate the values of k', k'', and m in Equation 2. Plots of the left-hand expression of Equation 2 versus $[H^+]^m$ were made at various m values until a best regression fit was obtained for both temperatures. Once this was accomplished, the values of k' and k'' could be obtained from the ordinate intercept and slope, respectively. The best regression fit for m based on the 70 and 100°C data was determined to be 0.25. Values of k' and k'' are given in Table II.

Table II. Calculated values for k' and k'' as a function of temperature for an A_E-stage conducted with a 90% ethanol medium.

Temperature (°C)	Rate Constant k' from Eq. 2 (s^{-1})	Rate Constant k'' from Eq. 2 (s^{-1} $M^{-0.25}$)	R^2	Data Points
70	1.47×10^{-5}	7.40×10^{-5}	0.98	4
100	6.98×10^{-5}	15.7×10^{-5}	0.99	5

The rate constants in Table II were fitted to an Arrhenius expression to yield:

$$k' = 3790e^{-6640/T} \quad (3)$$

$$k'' = 0.861e^{-3210/T} \quad (4)$$

The activation energies for k' and k'' from Equations 3 and 4 were determined to be 13.2 and 6.4 Kcal/mole, respectively. These activation energies for non-catalyzed and acid-catalyzed kinetic expressions are low for intrinsic chemical reactions to be the controlling factor for A_E delignification.

Evaluation of Delignification with Diffusion Theory

The low activation energies determined from the above kinetic analysis suggested that delignification is limited by physio-chemical factors such as diffusion. Diffusion theory has been used to describe the delignification observed with lignin leaching of unbleached kraft pulps under neutral [19,20] and alkaline conditions [21]. A similar approach was undertaken to determine whether or not A_E delignification is a lignin diffusion-controlled process.

The diffusion of lignin fragments from the fiber wall can be modeled as a porous flat plate if the following conditions are assumed: 1) the initial concentration of leachable fragments is constant across the fiber wall, 2) the diffusion of fragments occurs from both the outer and lumen wall, and 3) the concentration of fragments in the bulk solution is negligible in comparison to the concentration within the fiber [19,20].

Fick's Law of transient diffusion relates the concentration of lignin (C_L) as function of distance (x) and time (t):

$$D\left(\frac{\partial^2 C_L(x,t)}{\partial x^2}\right) = \frac{\partial C_L(x,t)}{\partial t} \quad (5)$$

where D is the effective diffusion coefficient [19,20]. Equation 5 can be solved if the following initial and boundary conditions are stipulated:

$$C_L(x,t) = C_L(0) \text{ for } -\ell < x < \ell \text{ at } t = 0 \quad (6)$$

$$C_L(x,t) \approx 0 \text{ for } -\ell \le x \le \ell \text{ for all } t \quad (7)$$

where $C_L(0)$ is the initial oxidized lignin concentration, and ℓ is one-half of the fiber wall thickness. The solution to Equation 5 can be expressed in terms of an average "leachable lignin" concentration across the fiber wall to yield [19,20]:

$$\gamma = \frac{C_L(t) - C_L(\infty)}{C_L(0) - C_L(\infty)} = 2\sum_{n=0}^{\infty}\left(\frac{2(-1)^n}{(2n+1)\pi}\right)^2 e^{\frac{-(2n+1)^2\pi^2\tau}{4}} \quad (8)$$

where τ is the dimensionless Fourier number (Dt/ℓ^2), and γ is the ratio of the remaining leachable lignin at time t to the total amount of leachable lignin. Tabulated values of γ versus τ for Equation 8 have been given by Favis [19].

Values of γ were computed based on the kappa numbers in Figure 4, $C_L(0)$ = 19.3 and $C_L(\infty)$ = 11.1 for the various temperatures, and the corresponding τ was determined. The value of D was determined from the corresponding τ based on a t of 5 hours and average softwood fiber wall thickness of 5 μm ($\ell = 2.5\text{x}10^{-4}$ cm) [19-21].

Figure 6 shows how the effective diffusion coefficient is affected by temperature. Diffusion increased somewhat linearly over the 25 to 70°C range; however, higher temperatures (≥70°C) greatly enhanced diffusion. Diffusion-controlled processes generally exhibit a linear dependency between the diffusion coefficient and temperature as is given by the Stokes-Einstein relationship [19-21]:

$$D \propto \frac{T}{\mu} \quad (9)$$

where μ is the solvent's viscosity. The behavior exhibited in Figure 6, however, is not uncommon for diffusion-controlled processes. Li and MacLeod [21], and Favis [19,20] noted dramatic increases in the diffusion coefficient of lignin during leaching of kraft brownstocks after ~70°C under alkaline and neutral conditions, respectively (Fig. 7). Likewise, Sprague [22] showed that the diffusion coefficients of dispersed dyes for cellulose acetate fibers increased linearly over the 40 to 80°C range, and suddenly increased above 80°C.

Several explanations have been given for the non-linear temperature dependency of diffusion, such as the one observed in Figure 7. Favis [19,20], and Li and MacLeod [20] attributed the sudden jump in lignin diffusion at 70°C to the thermal softening of lignin and hemicelluoses. However, this explanation cannot explain Spargue's observations [22] of dye diffusion into pure cellulose acetate fibers. Johansson [23] proposed that the dramatic increase in diffusion at ~70 to 100°C was due to the disruption of the hydrogen bonding network of water as the temperature approaches the boiling point. A similar disruption of the hydrogen bonding network with the ethanol-water system [24,25] could be occurring with the A_E-stage.

The diffusion coefficients in Figure 6 were correlated with temperature using an Arrhenius-type expression [21,26]:

$$D = AT^{0.5}e^{-E_d/RT} \quad (10)$$

where E_d is the activation energy of diffusion, and A is a pre-exponential factor. The value of E_d was calculated to be 13.2±2.0 Kcal/mole. This E_d is similar to diffusional activation energies calculated for diffusion-controlled processes such as lignin leaching of unbleached pulps (5.5 to 18 Kcal/mole [19-21]), and dyeing of cellulosic materials (11 to 35 Kcal/mole[22]).

One final analysis was performed to affirm that A_E delignification was diffusion-controlled. The Weisz-Prater criterion, F, represents the ratio of intrinsic chemical reaction and intraparticle diffusion:

$$F = \frac{r_l(t)\,\ell^2}{D\,\gamma(t)} = \frac{k\,\gamma(t)\,\ell^2}{D\,\gamma(t)} = \frac{k\,\ell^2}{D} \quad (11)$$

This simple criterion has been used to define if a process is chemical reaction or diffusion controlled [27]. Values of F that are less than 1 indicate that chemical reactions are controlling, while values of F greater than 1 indicate that particle diffusion is controlling. Calculated F values based on the A_E data obtained are all greater than 1 (Table III); these F values appear to further corroborate that A_E delignification is a diffusion-controlled process.

Table III. Weisz-Prater criterion, F, as a function of temperature for an A_E-stage conducted with a 90% ethanol medium with a 0.01 M $[H^+]$.

Temperature (°C)	Rate Constant k from Eq. 1 (s^{-1})	Diffusion Coefficient D from Eq. 8 (cm^2/s)	F from Eq. 11
25	0.646×10^{-5}	0.0328×10^{-12}	12.3
40	1.12×10^{-5}	0.0912×10^{-12}	7.69
55	2.75×10^{-5}	0.410×10^{-12}	4.19
70	3.78×10^{-5}	0.722×10^{-12}	3.27
85	6.20×10^{-5}	1.44×10^{-12}	2.69
100	15.0×10^{-5}	3.41×10^{-12}	2.75

Carbohydrate Degradation Kinetics and Selectivity

An important aspect of any bleaching stage is to effectively remove and/or modify the residual lignin without causing commensurable carbohydrate damage. Thus, the second phase of this study focused on how the A_E-stage affected pulp viscosity and strength. The aggressive conditions utilized during the A_E-stage to promote lignin dissolution may also accentuate the cleavage of acid-sensitive glycosidic bonds.

Figure 8 tracked carbohydrate damage over time with an A_E-stage performed with an acid concentration, $[H^+]$, of 10^{-2} M. A 70°C reaction temperature showed negligible viscosity reduction over time. However, increasing the temperature to 85 or 100°C augmented carbohydrate degradation, especially after 1 hour. Zero-span measurements were also performed on the above pulps to evaluate fiber strength (Fig. 9); these measurements closely mirrored the trends observed with viscosity. The viscosity data were coupled with the delignification data in Figure 4 to yield a selectivity plot (Fig. 10). This plot shows that A_E selectivity steadily decreases as the temperature of the stage is increased from 70 to 100°C.

Several kinetic analyses were performed to evaluate how reaction temperature and acid concentration affected pulp viscosity. The data in Figure 8 were initially fitted to an integrated first-order rate equation with respect to pulp viscosity (η):

$$ln\left(\frac{\eta(t)}{\eta(0)}\right) = -k_c t \qquad (12)$$

The activation energy for the rate constant in Equation 12, k_c was determined to be 24.2 Kcal/mole. This activation energy is similar to 20 to 30 Kcal/mole values reported for cellulose degradation during acid sulfite pulping [15-17].

Additional experiments were performed with different acid concentrations at 85 and 100°C (Table IV). Decreasing the acid concentration reduced the viscosity loss associated with the extraction stage. The overall rate constant, k_c, appeared to increase linearly as the acid concentration increased; this linear dependence between k_c and $[H^+]$ has been noted in the literature for acid degradation of cellulosic materials [16,28].

Table IV. Calculated k_c values from 5-hour viscosity values for an A_E-stage at various temperatures and acid concentrations. [Stage conducted with 90% EtOH; initial D-stage treated pulp viscosity of 23.8 cP.]

Temperature (°C)	$[H^+]$ (M)	Viscosity (cP)	Rate Constant k_c from Eq. 12 (s^{-1})
85	1×10^{-2}	16.0	2.11×10^{-5}
85	1×10^{-4}	21.2	0.643×10^{-5}
100	1×10^{-2}	8.7	5.59×10^{-5}
100	4×10^{-3}	14.1	2.89×10^{-5}
100	1×10^{-4}	21.1	0.661×10^{-5}

Equation 12 was modified to incorporate the catalytic $[H^+]$ term in the overall rate constant:

$$ln\left(\frac{\eta(t)}{\eta(0)}\right) = -(k_c' + k_c''[H^+])t \qquad (13)$$

where k_c' and k_c'' are the non-catalyzed and acid-catalyzed carbohydrate reactions, respectively. Equation 13 indicates that carbohydrate damage can occur through non-catalyzed reactions. This is not a surprising result. In their lignin leaching study, Li and MacLeod [21] reported a decrease in pulp viscosity when a kraft brownstock was subjected to high temperature extractions (≥100°C) in deionized water at near neutral pH conditions. The data contained in Table IV were used to determine how temperature affected the rate constants in Equation 13:

$$k_c' = 4.29x10^{-4} e^{-1520/T} \qquad (14)$$

$$k_c'' = 8.87x10^{9} e^{-10,500/T} \qquad (15)$$

The activation energies of k_c' and k_c'' were determined to be 3.1 and 20.9 Kcal/mole, respectively. Figure 10 compares the above model (Eq. 13 with Eqs. 14 and 15) to the data in Figure 8. The model slightly over predicts the viscosity drop with the 70°C data (Fig. 11); however, the model reasonably fits the data, considering the limited number of observations used to develop the model.

Improving A_E Bleaching Selectivity

Both carbohydrate (Eq. 13) and delignification (Eq. 2) models were developed to help predict A_E selectivity and to optimize process conditions. Figure 12 illustrates how the models were used to examine the effect of $[H^+]$ and reaction temperature on bleaching selectivity. Increasing the extraction temperature severely decreased the selectivity of the process at high $[H^+]$ (10^{-2} M). Yet, increasing the reaction temperature greatly improved A_E selectivity when the $[H^+]$ is low (10^{-4} M). This interesting selectivity relationship between acid concentration and temperature can be readily seen by comparing acid-catalyzed and non-catalyzed rate constants from the delignification and carbohydrate degradation models.

The results from the above analysis were utilized to better optimize the A_E-stage. Several A_E extractions were performed at various times at 130°C and 10^{-4} M $[H^+]$ (Table V). Approximately 40% of the incoming lignin was removed within the first hour of reaction using the above conditions. Essentially, all of the soluble lignin was removed within 5 hours. There was a nominal reduction in pulp viscosity and the zero-span strength. Overall, the higher temperatures and lower acid concentrations vastly improved A_E selectivity.

Table V. Changes in kappa, viscosity, and zero-span for an A_E-stage conducted at 130°C with 90% EtOH and 10^{-4} M $[H^+]$ with a D-stage treated pulp.

Reaction time (hrs)	Kappa Number	Viscosity (cP)	Zero-Span (Km)
0	18.8	23.8	20.9
1	11.1	22.7	19.3
2.5	10.6	22.8	19.2
5	9.3	22.1	19.1
14	9.3	-	-

A_E Comparisons to Aqueous Acid (A) and Caustic (E) Extractions

An aqueous A-stage, as was noted earlier in the preliminary investigation, was ineffective at delignifying a chlorine dioxide treated pulp. A-stages were conducted with an 18.8 kappa D-stage pulp at 70 and 100°C for 5 hours. Increasing the temperature an A-stage with 0.01 M $[H^+]$ from 70 to 100°C increased the kappa number reduction (17.1 vs. 15.1 kappa, respectively). The majority of this delignification occurred within the first hour; extending the extraction time did not increase lignin removal. Overall, an A-stage is not as proficient as an A_E-stage for lignin extraction.

Unlike the A-stage extraction, caustic extraction is very effective at removing the oxidized lignin from the D-stage

treated pulp. An E-stage conducted at 60°C for one minute can reduce a 19.5 kappa pulp to 12.1. The A_E-stage under selective conditions, on the other hand, requires higher temperatures (≥100°C) and longer periods of time to approach this level of lignin removal. However, the differences between the two extraction processes may indicate what mechanisms are responsible for the rapid lignin removal during aqueous bleaching. Additional research work is needed to elucidate these mechanisms [29].

Implications of A_E-Stage in an Organosolv-Based Bleaching Sequence

The results of this study indicate than an A_E-stage, based on process conditions, can be substituted for an E-stage [12] to extract lignin in an ethanol-based bleaching sequence. An appealing aspect of the A_E-stage is the elimination of alternating acid and alkaline bleaching stages. A partial organosolv bleaching sequence could be conducted on the acidic side using other oxidants besides chlorine dioxide, such as ozone and peracids. Effluents from oxidatitive and A_E stages can be combined and evaporated to recover the ethanol [30]. Recovered organic residues could be burned for their heating value or sold as potential high value byproducts similar to other organosolv lignins [1,30,31]. Another potential benefit of the ethanol-based sequence is the reduction of bleach plant water usage and its subsequent treatment.

CONCLUSIONS

This study investigated acid ethanol extraction (A_E) as an alternative to alkaline extraction for a chlorine dioxide treated brownstock for an "organosolv bleaching" sequence. Preliminary experiments showed that A_E lignin removal increased significantly as the temperature, ethanol content, and acid concentration were increased. A_E delignification appeared to be diffusion-controlled based on kinetic and diffusion theory analyses. Cellulose degradation and fiber strength loss for an A_E treatment were accentuated when the $[H^+]$ in the media was high (~10^{-3} to 10^{-2} M). Preliminary kinetic models for lignin and carbohydrate removal were developed to predict bleaching selectivity. The models showed that selectivity could be improved by decreasing the $[H^+]$ to ~10^{-4} M and increasing the reaction temperature to >100°C; experiments performed at these conditions confirmed the predictions. However, further experimental work is needed to refine the kinetic models to increase their accuracy. The results of this study suggested that an A_E-stage can be used as an alternative extraction method to caustic extraction in an ethanol-based organosolv bleaching sequence.

EXPERIMENTAL PROCEDURES

A thoroughly washed conventional softwood kraft pulp (southern pine) was obtained from a mill and had a kappa number of 29.3. Aqueous chlorine dioxide bleaches were performed on the pulp at the given conditions: 1.79% ClO_2 on o.d. pulp (0.16 kappa factor), 3.0% consistency, initial pH of 4.2 prior to ClO_2 addition, 45°C, and 30 minutes reaction time. [A 1 M HCl solution was used to acidify the pulp.] After the ClO_2 treatment, the pulp was washed with copious amounts of deionized water until the filtrate was clear. The resulting treatment yielded a pulp with kappa of 18.8 to 19.5, and a bleach filtrate with a 2.4 pH and no residual ClO_2.

Acid ethanol extractions were performed on 2.5 o.d. gram samples of the aqueous D-stage treated pulp. Experiments were conducted at low consistencies (0.50 to 1.25%) in 90% ethanol medium unless otherwise noted. Low temperature reactions (≤70°C) were conducted in sealed containers and were heated using a water bath. High temperature reactions (≥70°C) were performed with a 300 mL Teflon-lined Parr bomb reactor heated by an oil bath. Generally, the high temperature reactions (≥100°C) required 10 minutes to heat up to the specified reaction temperature. The pulps were extracted for the required period, cooled to 65 to 70°C (if needed), and drained of extraction effluent to ~25% consistency.

Micro-kappa number analyses (TAPPI Useful Method UM-246) were performed on the dried samples of the extracted pulps. Pulps subjected to dry zero-span measurements (TAPPI Standard T-231 cm-85) were washed with an aqueous sodium bicarbonate solution (~8.5 pH) to neutralize the residual acid from extraction. Unused paper strips from the zero-span analyses were utilized for pulp viscosity measurements (TAPPI Standard T-230 om-89).

Alkaline extraction runs with the D-stage treated pulp were conducted with the appropriate medium at the following conditions: 2.58% NaOH on o.d. pulp, 10% consistency, and 60°C. Additional details of alkaline extraction experiments have been reported in our previous study [12].

NOMENCLATURE

Bleaching stages

A	aqueous acid extraction stage
A_E	acid ethanol extraction stage
D	chlorine dioxide stage
E	caustic extraction stage

General

$[H^+]$	acid concentration, (M, moles/L)
R	ideal gas constant, (Kcal/mole•K)
T	temperature, (°C or K)
t	time, (s)

Delignification

A	pre-exponental factor for Arrhenius-type expression for diffusion, (Kcal/mole•$K^{0.5}$)
$C_L(t)$	average lignin concentration in the fiber at time t, (denoted by kappa number)
D	effective diffusion coefficient, (cm^2/s)
D_T/D_{20}	relative diffusion coefficient, ratio of effective diffusion coefficient at some T to effective diffusion coefficient at 20°C
E_d	diffusional activation energy, (Kcal/mole)
F	Weisz-Prater criterion [Eq. (11)]
$\gamma(t)$	Ratio of removable lignin at time t to total amount of removable lignin
k	overall delignification rate constant, (s^{-1})
k'	non-catalyzed delignification rate constant, (s^{-1})
k''	acid-catalyzed delignification rate constant, (s^{-1} $M^{-0.25}$)

ℓ	one-half average fiber wall thickness, (cm)
m	exponent
$r_l(t)$	rate of lignin removal at t, $d\gamma/dt$, (s^{-1})
τ	Fourier Number, (Dt/ℓ^2)
x	distance from the fiber wall center, (cm)

Carbohydrate Degradation

$\eta(t)$	pulp viscosity at time t, (cP)
k_c	overall carbohydrate degradation rate constant, (s^{-1})
k_c'	non-catalyzed carbohydrate degradation rate constant, (s^{-1})
k_c''	acid-catalyzed carbohydrate degradation rate constant, (s^{-1} $\underline{M}^{-1}$)

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REFERENCES

1. Hergert, H.L. and Pye, E.K. *1992 TAPPI Solvent Pulping Symp.,* Boston, MA, TAPPI Proc., p. 9 (1992).
2. Lora, J.H. and Aziz, S. *Tappi J.* 68(8):94 (1985).
3. Borgards, A., Pratt, R., Kordsachia, O., Odermatt, J., and Hunter, W.D. *1993 TAPPI Pulping Conf.,* Atlanta, GA, TAPPI Proc., p. 629 (1993).
4. Brogdon, B.N. and Dimmel, D.R., *J. Wood Chem. Tech.* 16(3):297 (1996).
5. McDonough, T.J. *Tappi J.* 76(8):186 (1993).
6. Ni, Y. and van Heiningen, A.H.P. *Tappi J.* 79(3):239 (1996).
7. Ni, Y. and Nu, Q. *J. Appl. Polym. Sci.* 57:1441 (1995).
8. van Heiningen, A.R.P. and Ni, Y. U.S. Pat. #5,354,423 (Oct. 11, 1994).
9. Kang, G.J., Ni, Y., and van Heiningen, A.R.P. *82nd Annual Meeting, Tech. Section CPPA*, CPPA Proc., p. B303 (1996).
10. Solinas, M. and Murphy, T. *Pulp & Paper* 70(3):133 (1996).
11. Sundquist, J. and Poppius-Levlin, K. *1992 TAPPI Solvent Pulping Symp.,* Boston, MA, TAPPI Proc., p. 45 (1992).
12. Brogdon, B.N., Dimmel, D.R., McDonough, T.J., and Bryant, P.S. *1996 Intl. Pulp Bleaching Conf.*, Washington, DC, TAPPI Proc., p. 541 (1996).
13. Brogdon, B.N., Dimmel, D.R., and McDonough, T.J. *1996 TAPPI Pulping Conf.,* Nashville, TN, TAPPI Proc., p. 35 (1996).
14. Morrison, R.T. and Boyd, R.N. *Organic Chemistry,* Fourth Ed., John Wiley & Sons, Inc., New York, Chapt. 19 (1991).
15. Rydholm, S.A. *Pulping Processes*, Interscience Publishers, New York, Chapt. 9 (1965).
16. Ingruber, O. "Process Measurement and Control" In *Pulp and Paper Manufacture, Vol. 4: Sulfite Science & Technology*. Ed. by O. Ingruber, M. Kocurek, and A. Wong. Joint Textbook Committee of the Paper Industry, Atlanta (1985).
17. Vuorinen, T., Teleman, A., Fagerström, P., Buchert, J., and Tenkanen, M. *1996 Intl. Pulp Bleaching Conf.*, Washington, DC, TAPPI Proc., p. 43 (1996).
18. Ni, Y., Kubes, G.J., and van Heiningen, A.R.P. *J. Pulp Paper Sci.* 16(1):J13 (1990).
19. Favis, B.D. *The Leaching of Lignin Macromolecules from Pulp Fibers During Washing*. Ph.D. Disertation, McGill University, Montréal (1981).
20. Favis, B.D., Choi, P.M.K., Adler, P.M., and Goring, D.A.I. *Trans. of the Tech. Section, CPPA* 7:35 (1981).
21. Li, J. and MacLeod, J.M. *J. Pulp Paper Sci.* 19(2):J85 (1993).
22. Spargue, B.S. *J. Polymer Sci., Part C* 20:159 (1967).
23. Johansson, A. *J. Pulp Paper Sci.* 11(3):J78 (1985).
24. Coccia, A., Indovina, P., Podo, F., and Viti, K. *Chem. Phys.* 7:30 (1975).
25. Laiken, N. and Hemethy, G. *J. Chem. Phys.* 74:3501 (1970).
26. Wong, C.F. and Hayduk, W. *Can. J. Chem. Eng.* 68:849 (1990).
27. Pugliese, S.C. and McDonough, T.J. *Tappi J.* 72(3):159 (1989).
28. Hansen, S.M. *The Role of Solvent in Aqueous-Organic Solvent Delignifiction of Southern Pine.* Ph.D. Disertation, University of Alabama, University, p. 24 (1981).
29. Brogdon, B.N. *The Influence of Selected Organic Solvents on Chlorine Dioxide Bleaching*. Ph.D. Disertation, IPST, Atlanta, (in preparation).
30. Lora, J., Winner, S.R., and Pye, E.K. *AIChE 1989 and 1990 Forest Products Symp. Proc.* Ed. by J.D. Lisius, TAPPI Press, Atlanta, p. 35 (1992).
31. Lora, J. and Pye, E.K. *1992 TAPPI Solvent Pulping Symp.,* Boston, MA, TAPPI Proc., p. 27 (1992).

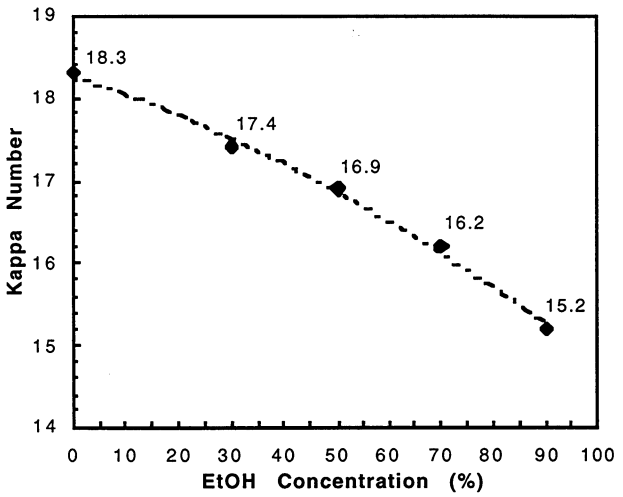

Figure 1. The influence of ethanol concentration on A_E delignification at the following conditions: 0.01 M $[H^+]$ in the medium, 70°C, and 5 hours reaction time. [Initial D-stage treated pulp kappa of 19.3.]

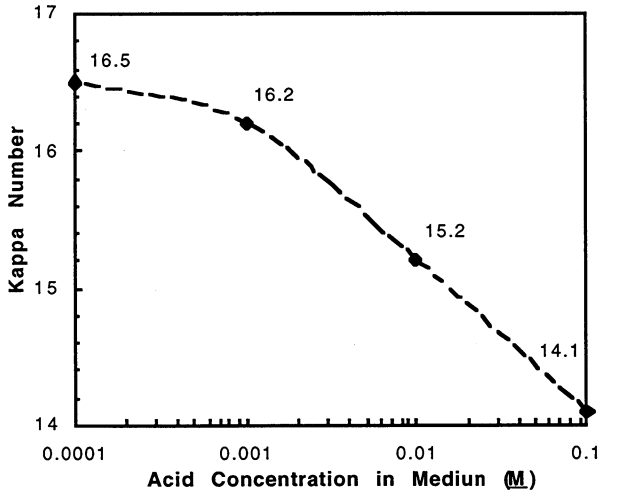

Figure 2. The influence of acid concentration ($[H^+]$) on A_E delignification at the following conditions: 90% EtOH medium, 70°C, and 5 hours reaction time. [Initial D-stage treated pulp kappa of 19.3.]

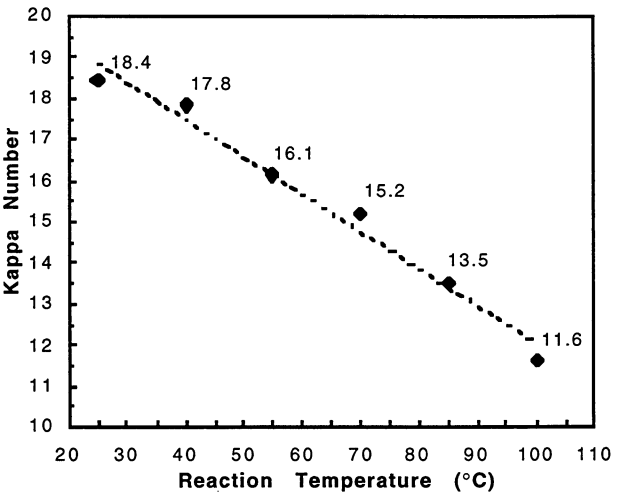

Figure 3. The influence of reaction temperature on A_E delignification at the following conditions: 90% EtOH and 0.01 M $[H^+]$ medium, and 5 hours reaction time. [Initial D-stage treated pulp kappa of 19.3.]

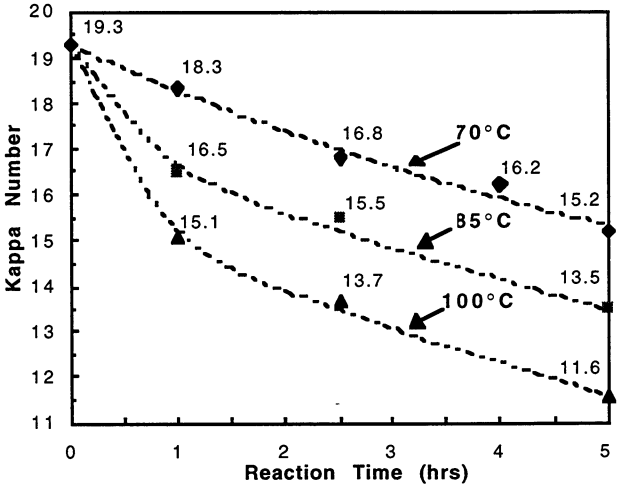

Figure 4. The influence of reaction temperature and time on A_E delignification at the following conditions: 90% EtOH and 0.01 M $[H^+]$ medium. [Initial D-stage treated pulp kappa of 19.3.]

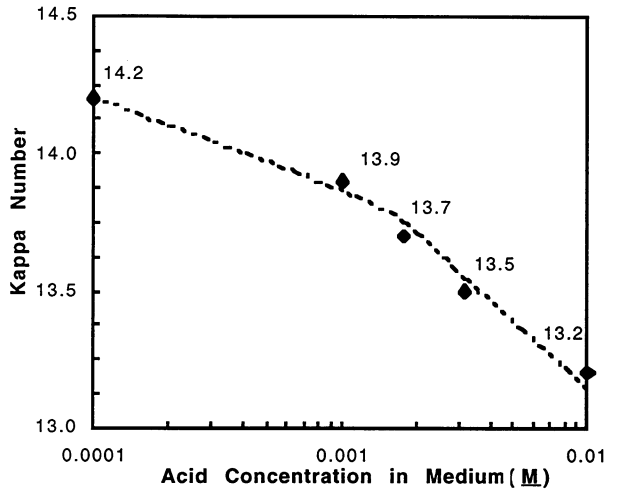

Figure 5. The influence of acid concentration ([H^+]) on A_E delignification at the following conditions: 90% EtOH medium, 100°C, and 2.5 hours reaction time. [Initial D-stage treated pulp kappa of 18.8.]

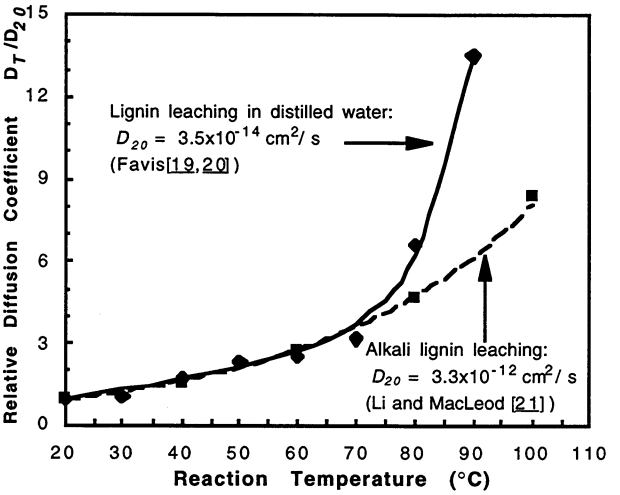

Figure 7. Reported relative effective diffusion coefficients (D) of lignin during lignin leaching under neutral and alkaline conditions with softwood kraft pulps [19-21].

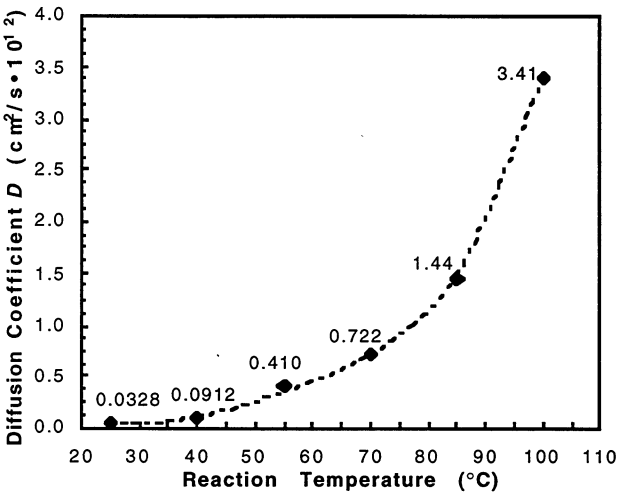

Figure 6. Calculated effective diffusion coefficients (D) of oxidized lignin at 5 hours reaction time. Conditions of the A_E-stage: 90% EtOH and 0.01 M [H^+]. [Initial D-stage treated pulp kappa of 19.3.]

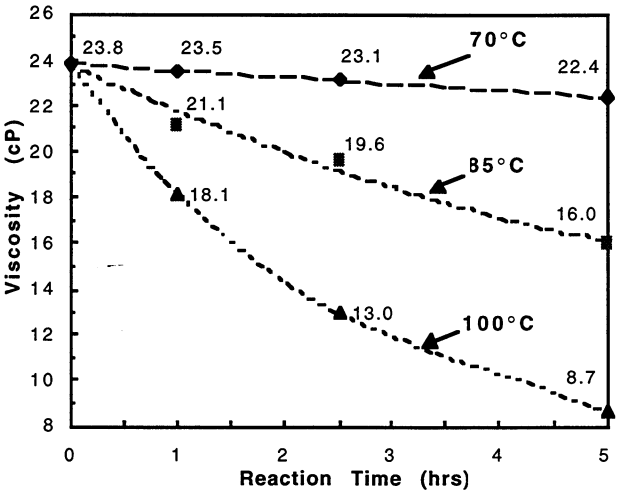

Figure 8. Observed carbohydrate degradation at various reaction temperatures for an A_E-stage conducted with 90% EtOH and 0.01 M [H^+] medium. [Initial D-stage treated pulp viscosity of 23.8 cP.]

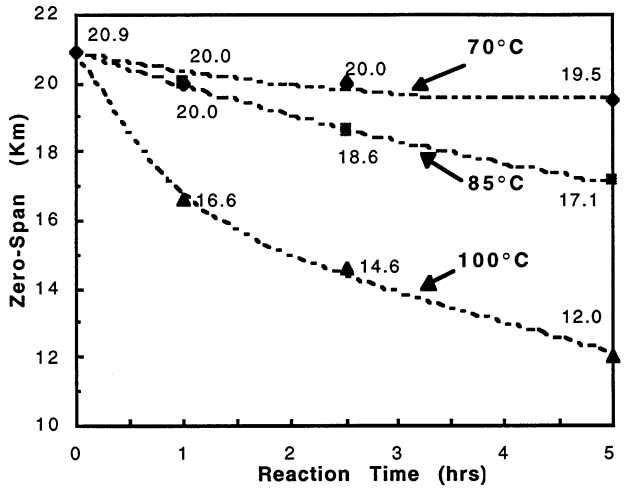

Figure 9. Observed fiber strength degradation at various reaction temperatures for an A_E-stage conducted with 90% EtOH and 0.01 M $[H^+]$ medium. [Initial D-stage treated pulp zero-span of 20.9 Km.]

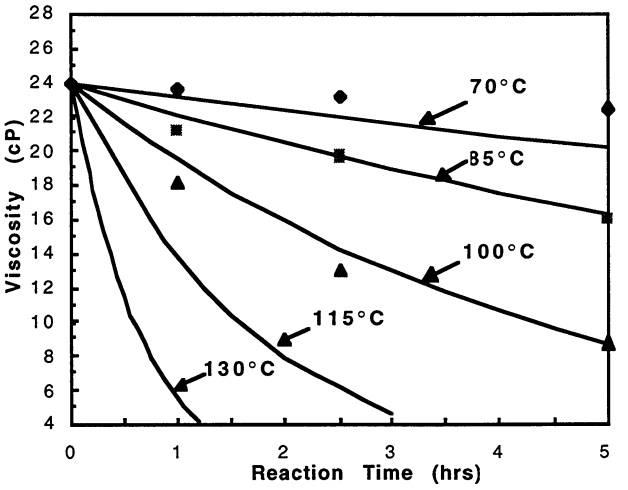

Figure 11. Predicted carbohydrate degradation (solid lines) from Eqs. 13 - 15 compared to the observed data in Fig. 7 (symbols) for an A_E-stage conducted with 90% EtOH and 0.01 M $[H^+]$ medium.

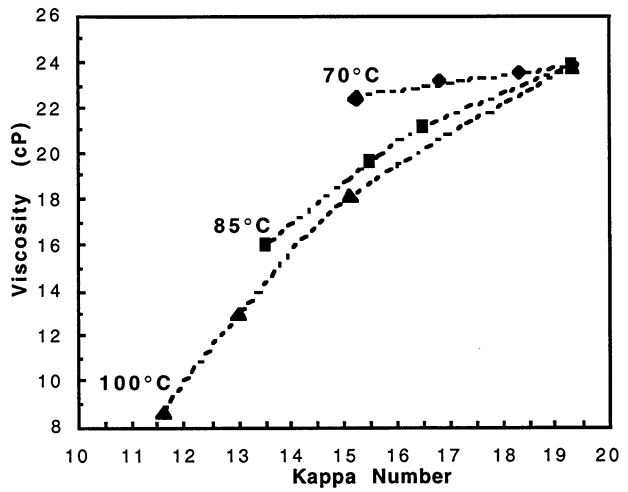

Figure 10. Selectivity plot at various temperatures for an A_E-stage conducted with 90% EtOH and 0.01 M $[H^+]$. [Initial D-stage treated pulp with 19.3 kappa and 23.8 cP viscosity.]

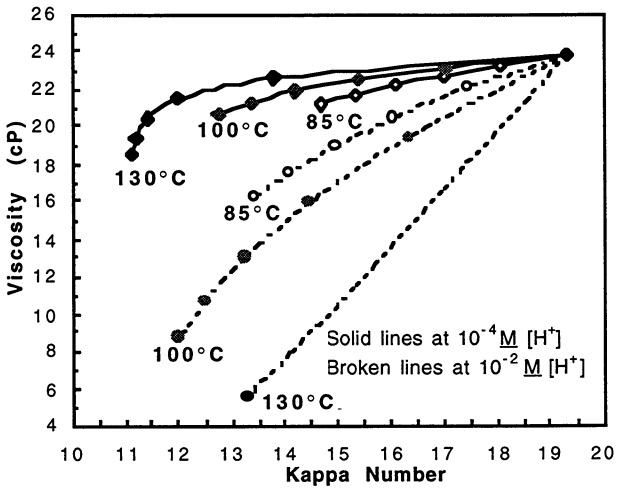

Figure 12. Predicted selectivites at various A_E-stage conditions with 90% EtOH media with the delignification and carbohydrate degradation kinetic models. Symbols are at one-hour reaction incriments.